THE EFFECT OF SIZE AND STRUCTURE OF FILLER PARTICLES ON PAPER PROPERTIES

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TIIVISTELMÄ

Tampereen ammattikorkeakoulu
Paperitekniikka
International Pulp & Paper Technology

HENNA RAJALA:
Täyteaineen partikkelikoon ja -rakenteen vaikutus paperin ominaisuuksiin

Opinnäytetyö 57 sivua, josta liitteitä 13 sivua
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Tässä opinnäytetyössä tutkittiin erään yrityksen toimeksiantona eri täyteaineiden koon ja rakenteen vaikutuksia paperi-teknisiin ominaisuuksiin. Tutkimusta varten valmistettiin ja testattiin laboratorioarkkeja eri täyteainepitoisuuksilla. Täyteaineita käytetään nykyään yhä enemmän paperinvalmistuksessa. Täyteaineiden käytön etu kuituihin verrattuna on niiden edullinen hinta. Lisäksi täyteaineet parantavat paperin painettavuusominaisuuksia. Täyteaineiden käyttäminen kuitenkin heikentää joitakin paperin ominaisuuksia, kuten lujuuksia. Työn teoriaosassa keskitytään täyteaineiden käyttöön, etuihin ja haittoihin sekä yleisimpiin markkinoilla esiintyviin täyteaineisiin. Lisäksi teoriaosassa käydään hieman läpi täyteaineiden kehityssuuntia.

Työ sisältää luottamuksellista tausta-aineistoa.

Asiasanat: täyteaineet, paperin ominaisuudet, partikkelikoko, partikkelirakenne

ABSTRACT

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Bachelor's thesis 57 pages, appendices 13 pages
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The aim of this thesis was to study the effects of size and structure of filler particles on paper technical properties. The work was carried out by making laboratory sheets with different filler levels and testing the sheets. This thesis is done as an assignment of a certain company. Fillers are used to replace fibers because one great benefit of fillers compared with fibers is their low price. Fillers improve the printing quality of the paper. On the other hand, use of fillers weakens some technical properties of the paper, like strength properties. In theory part of this thesis the use, the benefits and the drawbacks of fillers are examined. In addition, some future developments of fillers are studied.

The thesis contains confidential background material.

Key words: fillers, paper properties, particle size, particle structure

CONTENT

1 INTRODUCTION

This thesis consists of a theory part and an experimental part. In theory part the focus is on the behavior and effects of fillers but different kinds of filler types and their properties are also gone through.

2 FILLERS IN GENERAL

Paper fillers are fine, white pigment powders and they are made directly or chemically from natural minerals. The aim of using fillers is to fill in spaces between fibers. Some of the key fillers used in paper making are kaolin, ground calcium carbonate (GCC), precipitated calcium carbonate (PCC), talc, gypsum, titanium dioxide and synthetic silicates. (Häggblom-Ahnger & Komulainen 2006, 37; Krogerus 2007, 56.)

The use of fillers has been increasing constantly. Most papers contain fillers but the amount depends mainly on paper grade. The average content of added fillers is from 20 % to 35 % of the paper furnish. One important reason for the use of fillers is lower cost compared to fibers. However, specialty pigments such as titanium dioxide are used less due to their expensiveness. (Häggblom-Ahnger & Komulainen 2006, 37; Krogerus 2007, 57.) Typical filler contents in different paper grades are listed in figure 1.

Examples of paper product filler contents

Newsprint	0-15 %
SC gravure paper	20-32 %
LWC base paper	6-10 %
Wallpaper	8-15 %
Mechanical catalogue paper	5-10 %
Wrapping base paper	5-20 %
Woodfree printing paper	10-25 %
Woodfree writing paper	10-25 %
Coorugated board	2-10 %
Wallpaper board	2-10 %

FIGURE 1. Filler contents in different paper grades (Knowpap 2010)

Fillers are mainly used in printing and writing papers. As it is shown in figure 1, SC paper can contain over 30 % of fillers. Also woodfree papers can have relatively high filler content. There are also some filler in newsprint because of the recycled pulp used in the process. Decrease of bulk and stiffness restrict the use of fillers in paper boards. (Häggblom-Ahnger & Komulainen 2006, 42.)

There are different ways for fillers to be situated in the fiber network of paper (figure 2). The most important factors affecting the filler positioning are the filler properties (size and shape of the particles, characteristic surface), the structure of fiber network and forming conditions. (Krogerus 2007, 65.)

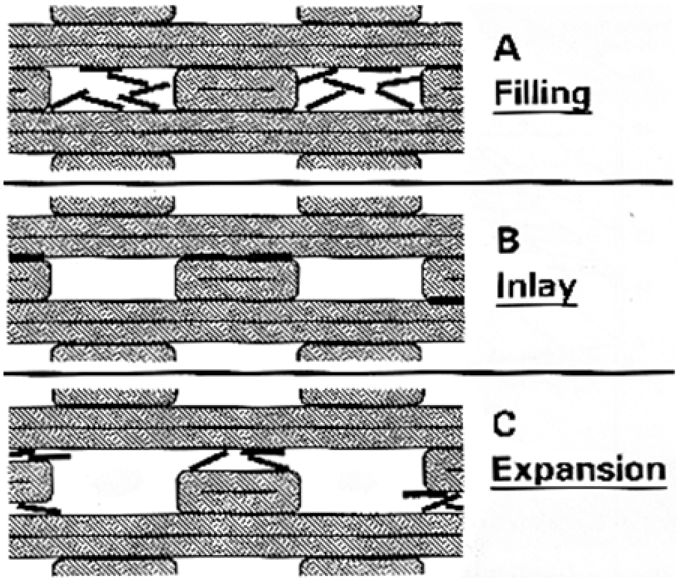

FIGURE 2. Options for filler positioning in fiber network (Krogerus 2007, 65)

The fiber network has plenty of voids. As it is shown in figure 2, fillers may fill up these empty spaces without affecting the structure. They may also penetrate into the fiber network (inlay and expansion) and break bonds. Usually finer particle size means higher amount of particles which predicts less bonding.

Fillers are delivered to the paper mill as a powder (when dispersing is carried out at the mill) or as a finished slurry. Because of the surface chemical properties of fillers, different dispersion chemicals are usually required during dispersing to facilitate dispersion and prevent the reformation of already disintegrated agglomerates. (Knowpap 2011.)

2.1 Advantages of fillers

One of the most important benefits of using fillers is their positive effect on optical properties (opacity, brightness, light scattering) and along with that on the appearance of the paper.

Due to their higher degree of diffused reflection and low bonding capacity, fillers improve paper opacity. Brightness is improved because of the purity of the pigment. The total light scattering is the result of a proportional input of both fibers and pigments. Fillers open the structure of the fibers so light scattering is improved because of the reduction of fiber bonding. (Krogerus 2007, 69; Paltakari, J. 2011.) The light scattering efficiency of pulp and different fillers is shown in figure 3.

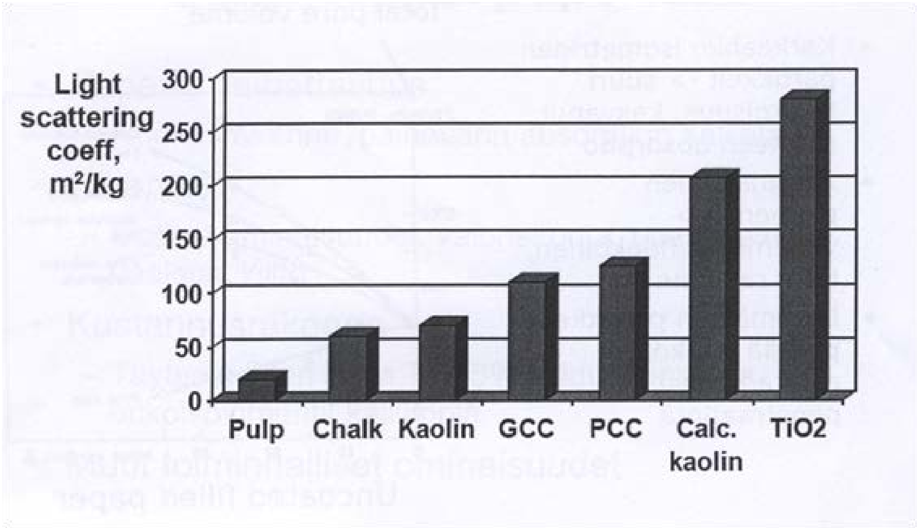

FIGURE 3. Light scattering efficiency of fillers (Paltakari 2011)

As it is shown in figure 3, titanium dioxide and calcined kaolin scatter the light best (over 200 m^2/kg). Pulp, chalk and ordinary kaolin have the lowest values in light scattering efficiency, less than 100 m^2/kg.

Fillers also affect positively papers surface properties which are important in printing and coating process. Smoothness and gloss are generally improved by fillers, particularly for calendered papers. Also the absorption of water and ink is more even in the presence of fillers. Some specialty fillers such as calcined clay are able to absorb the printing ink, in other words they can prevent the penetration through the paper sheet. (Krogerus 2007, 69.)

2.2 Disadvantages of fillers

The strength properties of the paper are highly dependent on fibers and above all fiber bonding capability. As the share of fillers increases, the strength of the sheet decreases because of the inability of fillers to form relevant bonds to fibers or to combine notably fiber-to-fiber bonding. By replacing fibers with fillers, the strength will also decline as the network per unit volume is too low in fibers. So it is challenging to maintain a sufficient strength level when increasing the filler content. (Krogerus 2007, 66.) Figure 4 shows the effect of filler amount on tensile index and tear index.

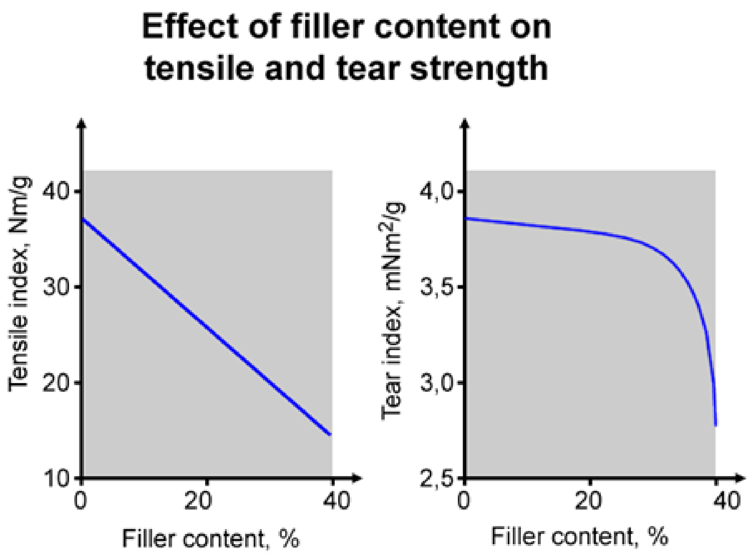

FIGURE 4. Effect of filler content on tensile index and tear index (Knowpap 2010)

As it can be seen from figure 4, tensile strength decreases in a linear fashion, whereas tear strength starts to decrease remarkably only in higher filler loading.

Because the density of fillers is usually higher than the density of fibers, paper bulk will decrease when increasing the filler content at constant grammage. For paper and paper board it is usually desirable to have low density and high bulk which also correlates with good opacity, high stiffness and high tear strength. (Häggblom-Ahnger & Komulainen 2006, 83; Krogerus 2007, 65.)

The two-sidedness of paper is another significant drawback of using high amounts of fillers. The problem is common on the machines with asymmetric water drainage on the wire section. The structural difference between the sides of the paper leads to variations in brightness, smoothness, color and gloss between the two sides. Two-sidedness can also cause unevenness in ink absorption in printing. By taking notice of the correct application of calendering techniques and the appropriate dewatering machinery, two-sidedness can be somewhat corrected. (Krogerus 2007, 68.)

3 PROPERTIES OF FILLERS

There are different kinds of properties for determining the nature of filler. Index of refraction tells about light scattering and chemical inertness refers to solubility. Absorption properties, brightness, color, charge and attack are also properties to describe filler. One of the most important is still morphology which involves particle size, particle size distribution, particle shape and specific surface. In this research the focus is on particle size and particle shape which are properties affecting every aspect of the use of filler and the success of many applications. (Turku 2010.)

A term called equivalent spherical diameter is used in the measurement of particle size. This measurement is based on sedimentation which is calculated under Stokes' law. However, the defects of this method are the unawareness of specific surface and true measures of the particles, and density of aggregated particles. (Turku 2010.)

3.1 Effect of particle size and shape on paper properties

The effects of smaller particle size of the filler on different paper properties are shortly listed in figure 5.

(+)	0	(-)
↑ Paper brightness	0/ ↓ Bulk	↓ Paper strength
↑ Opacity	0/ ↓ Stiffness	↑ Size demand
↓ Dusting	0/ ↓ Porosity	
↓ Wire abrasion		

FIGURE 5. Benefits and disadvantages of smaller particle size on paper properties (modified from Turku 2010)

As it is shown in figure 5, brightness and opacity are improved. Due to smaller particle size there is less wire abrasion and dusting. On the other hand, paper strength decreases and size demand increase. Bulk, stiffness and porosity are either decreased or remained unchanged as the particle size decreases.

Because fillers are unable to form significant bonds to fibers, strength properties which depend on interfiber bonding decrease when fillers are introduced into the sheet structure. The three-dimensional figure 6 illustrates how filler loading and particle size affect tensile index in fine paper sheets.

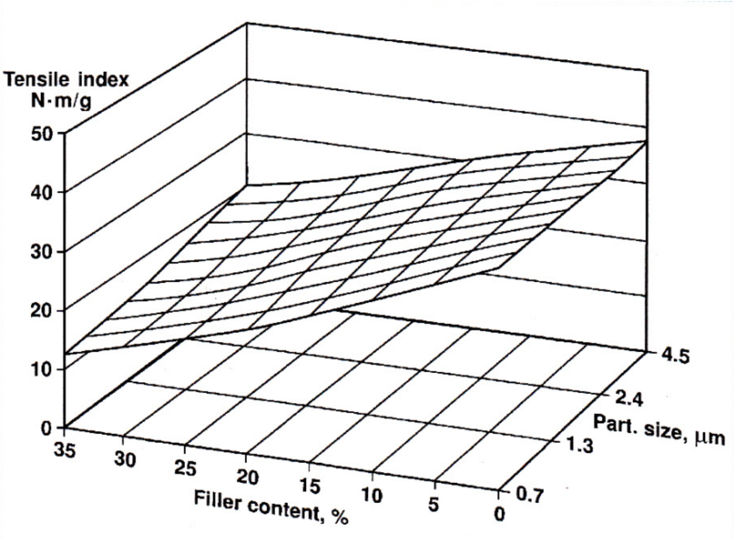

FIGURE 6. Tensile index as a function of filler content and particle size (Krogerus 2007, 66)

Figure 6 shows that the joint affect of filler loading and particle size effect on tensile index. Not only increased filler amount but also a finer particle size impairs tensile strength.

As it is mentioned before, fillers have an almost exclusively positive effect on optical properties. Very small and flat particles are effective in achieving opacity. The effect of fillers on paper brightness depends on the ratio of fiber and filler brightness.

Fillers themselves have an ability to refract light but the impact depends on ideal particle size which is in the area of 0.2-2 μm. (Paltakari, J. 2011.) Figure 7 shows the effect of particle size on light scattering and where the optimal light scattering value is achieved. S-value in figure 7 describes light scattering.

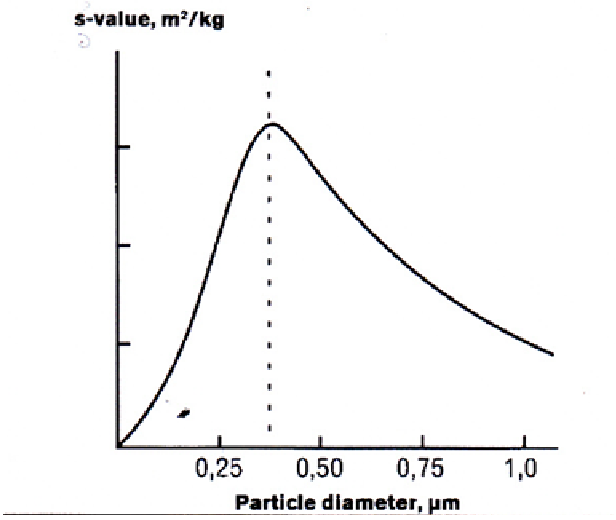

FIGURE 7. Effect of particle diameter on light scattering (Turku 2010)

Fillers improve paper gloss. Especially small particles with laminar structure make the paper glossier. The effect of filler size on paper gloss is shown in figure 8. More there are smaller particles the better the gloss is.

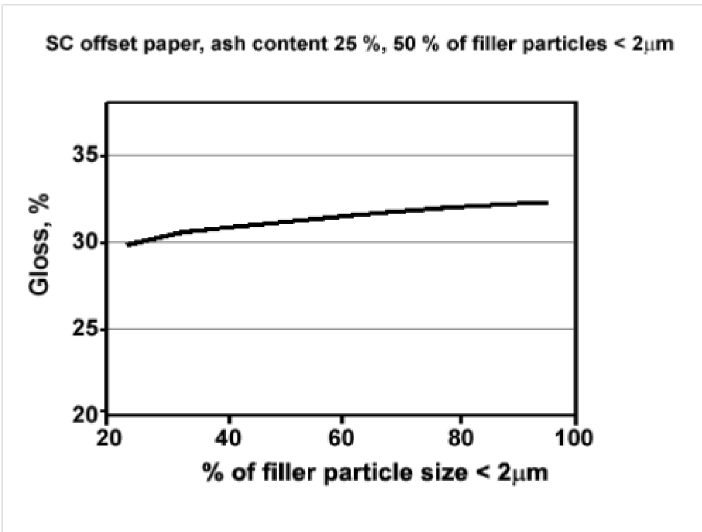

FIGURE 8. Effect of filler particle size on paper gloss (Knowpap 2010)

The impact of filler shape on paper gloss can be seen from figure 9, where aspect ratio refers to the flatness of filler particle, in other words the platier the structure the higher the gloss. It is also examined that a rod-shaped form combined to platy structure improves gloss. (Turku 2010.)

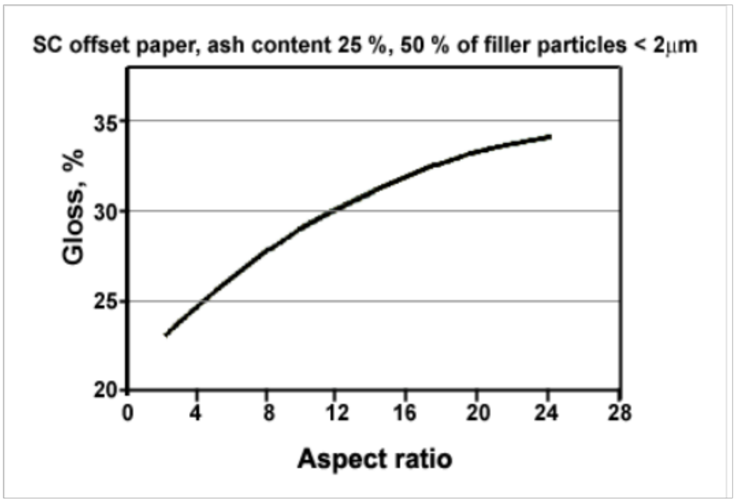

FIGURE 9. Effect of filler particle shape on paper gloss (Knowpap 2010)

In addition to smoothness and gloss, low porosity is also important for the printability of coated paper. High porosity leads to a loss in print density. The impact of fillers on porosity depends on the particle size and shape of the filler. As it is illustrated in figure 10, coarse fillers (such as calcium carbonate) will increase porosity, while fine fillers with a laminar structure will decrease porosity. (Krogerus 2007, 69.)

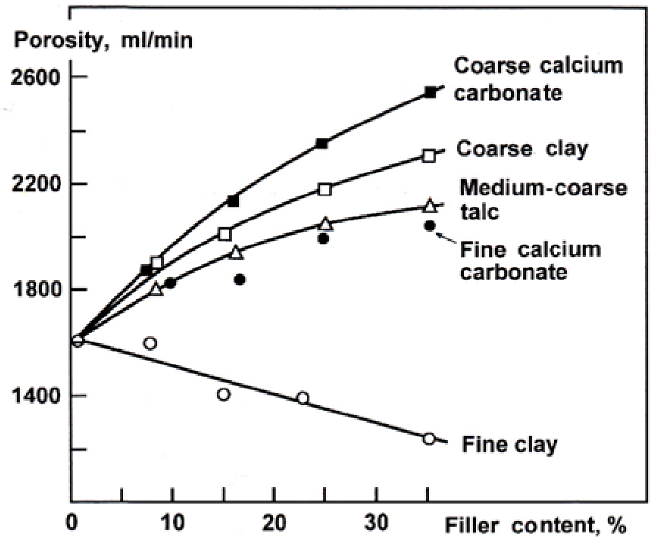

FIGURE 10. Impact of different fillers on paper porosity (Krogerus 2007, 69)

There is a clear connection between porosity and air permeability which is used to predict the penetration of liquids into the sheet. It is the most significant general surface effect of fillers on sheet properties. Figure 11 shows air permeability as a function of particle size and shape when chalk and kaolin are compared. It can be interpreted from figure 11 those platy particles clearly give lower air permeability at a given size.

Generally the reducing of air permeability improves printing properties. (Häggblom-Ahnger & Komulainen 2006, 89; Krogerus 2007, 70.)

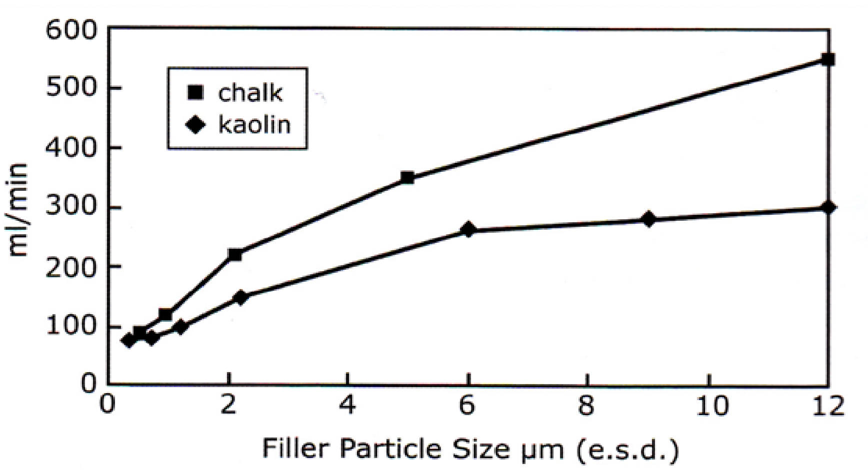

FIGURE 11. Air permeability as a function of filler particle size and shape (Krogerus 2007, 70)

Paper bulk is increased when particle size is increased to a maximum extent (figure 12). The progress stops when particle size reaches 3 µm.

FIGURE 12. The impact of average particle size on bulk (Turku 2010)

As the density of fillers is generally higher than the density of fibers, paper thickness will increase with an increase in filler content. A blocky filler such as chalk will increase thickness more than a platelet-type filler (e.g., clay and talc), although the size of a particle plays more important role. (Krogerus 2007, 65-66.)

3.2 Effect of particle size and shape on paper making process

Fillers and fiber raw materials behave differently in many parts of the paper making process and these differences are due to the different properties of fillers and fibers. However, fillers are not actually used as process functions, but to affect the properties of the finished product, such as price and printability. (Knowpap, 2010)

Good retention is always one of the targets in paper making. Fillers can be retained mechanically into the web or chemically with the help of polymers. Poor filler retention means inefficient use of fillers and high loading of circulation and waste waters. Filler retention can be affected by many parameters, for example the furnish composition and the construction of the drainage elements. (Krogerus 2007, 72.) By increasing the particle size the retention is evidently improved (figure 13).

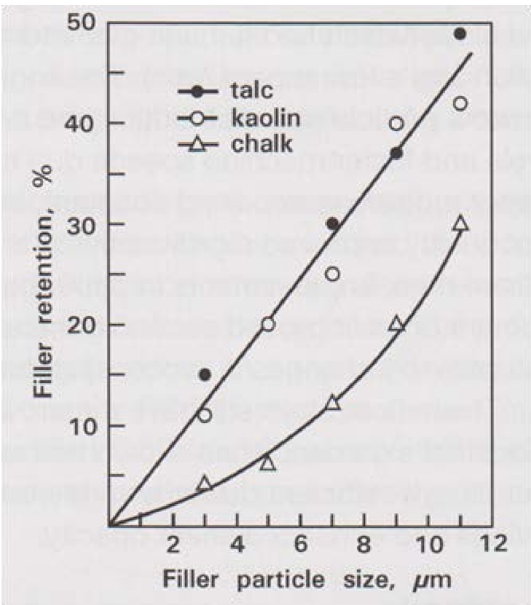

FIGURE 13. Filler retention vs. particle size for fillers of different shape (Krogerus 2007, 73)

As it can be seen from figure 13, particle shape also affects retention. Kaolin and talc platelets display better retention than spherical chalk.

4 FILLER TYPES

There is a wide range of different fillers available on the market. Fillers can vary a lot from each other. Physical properties of most used fillers are shown in table 1.

TABLE 1. Physical properties of typical filler pigments (Krogerus 2007, 59)

Property	Kaolin	Talc	GCC	PCC
	$Al_4Si_4O_{10}(OH)_8$ **Triclinic hexagonal platelets**	$Mg_3Si_4O_{10}(OH)_2$ **Monoclic, lamellae**	$CaCO_3$ **Trigonic, rhombohedral**	$CaCO_3$ **Scalenohedral, rhombohedral aragonite**
Density, kg/dm^3	2.7	2.8	2.7	2.7
Refractive index	1.56	1.57	1.6	
Hardness (Mohs scale)	2–2.5	1–1.5	3	
Brightness ISO, % (e.g., filler for SC paper)	80–90	Ca. 85	86–97	95–99
Optical constants,				
S, m^2/kg	100–180	Ca. 110	100–300	150–350
K, m^2/kg	1–3		0.5–3	0.02–0.4
Particle size distribution, %				
< 5 µm	75	45	90	100
< 2 µm	48	16	40	70
Zeta-potential, mV	-24 (pH 7)	-19 (pH 9)	-26 (pH 9)	+5 (pH 9)
Ignition loss, %				
600 °C	11	5.5	0-2	0
925 °C	12	6.3	42	42
pH (10 % suspension)	5	7–9	9–11	9–11

Physical properties of some specialty fillers are listed in table 2.

TABLE 2. Physical properties of selected specialty fillers (Krogerus 2007, 62)

4.1 Kaolin

Kaolin is the most commonly used filler right after calcium carbonate. It is a natural mineral which occurs in clay. Small and flat kaolin particles improve retention, opacity, gloss and smoothness which are requirements for good printability. On the other hand the platy form sadly slows down dewatering and evaporation in drying section. Kaolin is easy to handle and suspend. It does not foam and it is suitable for neutral and acid conditions alike. (Häggblom-Ahnger & Komulainen 2006, 39; Krogerus 2007, 58; Turku 2010.) The laminar structure of kaolin can be seen from figure 14.

FIGURE 14. The laminar structure of kaolin (Knowpap 2010)

Kaolin occurs in various parts of the world but the main deposits are located in the United Kingdom, the United States and Brazil. The European kaolin is of the primary type where the particles are usually very platy and coarse. Whereas the American kaolin is of the secondary type which means that in time the material has moved along with water and therefore the particles are finer and less platy. Because of the availability of various particle sizes and brightnesses, different kinds of kaolin types are made for different purposes. (Häggblom-Ahnger & Komulainen 2006, 39; Krogerus 2007, 58.)

4.2 Ground Calcium Carbonate

The natural product ground calcium carbonate (GCC) is a common filler in Europe and it is refined either from chalk, marble or limestone. Chalk is a sedimentary rock of soft and porous texture and the color varies from white to slender gray. Marble is a metamorphous rock with yellow or brownish red streaks which are caused by iron oxide or other agents. Limestone is harder and less porous than chalk. Both marble and limestone have very high brightness and purity. (Krogerus 2007, 58-59.)

The benefit of using GCC in the process is drainage which is improved due to roundish but still jagged shape of GCC particles. GCC also improves opacity and provides higher brightness than kaolin. In addition, strength tends to be quite high when the need of alum is minor and filler loadings are higher. (Turku 2010.) The form of GCC particles can be seen from figure 15.

FIGURE 15. Form of GCC particles (Knowpap 2010)

Acid conditions restrict the use of calcium carbonates. After the dissolution where calcium carbonate degrades to carbon dioxide and lime milk, pH rises far over 7. This involves the yellowing of the lignin and difficulties in the wet end chemistry caused by disturbing agents dissolved from the lignin. Therefore GCC is used only in neutral processes. (Häggblom-Ahnger & Komulainen 2006, 40.)

4.3 Precipitated Calcium Carbonate

Totally synthetic product PCC is made from limestone which is burned and then reprecipitated with carbon dioxide. Due to slightly cationic nature of PCC sludge, there is no need for anionic dispersing agents which bite the retention. PCC is widely used around the world. (Häggblom-Ahnger & Komulainen 2006, 40; Krogerus 2007, 60.) Figure 16 shows a simplified manufacturing process of PCC.

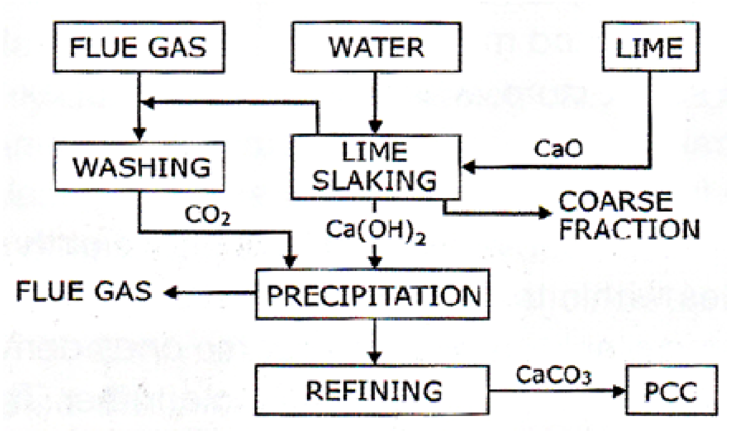

FIGURE 16. Flowsheet of the manufacturing process of PCC (Krogerus 2007, 60)

Aragonite and calcite are crystal forms of PCC. Aragonite is a needle-like form of PCC. Calcite form is divided into rhombohedral and scalenohedral agglomerates. The achievement of certain form depends on manufacturing conditions where at least temperature, time, gas run, concentration and additives are considered to be important. Different crystal forms of PCC are shown in figure 17. (Turku 2010.)

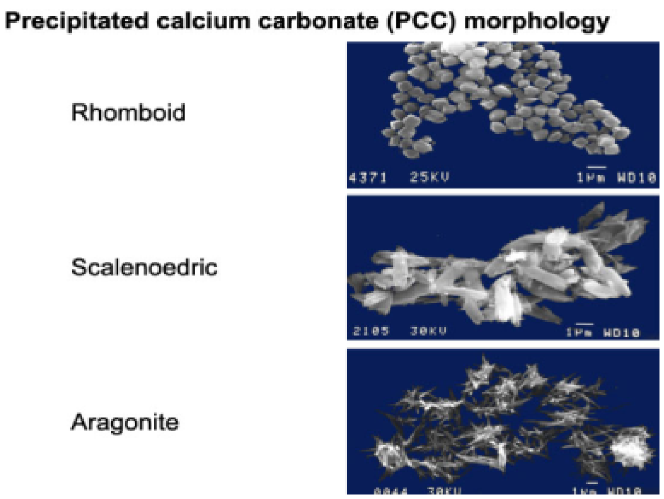

FIGURE 17. Different crystal forms of PCC (Knowpap 2010)

Despite the higher price the use of PCC is constantly growing. The synthetic manufacturing process offers high brightness without decreasing opacity and specific mineral properties, for example small particle size distribution and customized particle shape. Brightness of PCC varies between 94 % and 97 % and because of a large light scattering it can be increased without decreasing opacity. Other benefits of PCC are improved bulk and good retention. However, PCC also reduces dewatering and decreases strength when compared to coarse and platy filler. (Häggblom-Ahnger & Komulainen 2006, 40; Turku 2010.)

4.4 Talc

As filler talc is platier than kaolin, it has a soft nature and it is light in color (figure 18). Talc is made by separating the talc mineral from ore of soapstone. Talc is mined in the United States, in France and large amounts in Finland too. (Krogerus 2007, 58; Knowpap 2010; Turku 2010.)

FIGURE 18. Talc particles (Krogerus 2007, 60)

Talc resembles kaolin in many ways and they have same applications. The advantage of talc particles is a hydrophobic surface which is capable of adsorbing organophilic impurities from pulp and paper making processes. Therefore talc is used for example in resin control. Talc is well suited for gravure printing papers. Disadvantages of talc are foaming and a slight difficulty of elutriation. (Häggblom-Ahnger & Komulainen 2006, 39; Turku 2010.)

4.5 Calcined Kaolin

Calcined kaolin is made by processing carefully chosen rough kaolin to a very fine particle size. After this the product is calcined at very high temperature which can reach 1000 °C. Gloss and smoothness remain good because of the stability of flat shape of calcined kaolin particles (figure 19). Other advantages of calcined kaolin are improved printability and remarkably less show-through. (Krogerus 2007, 62; Turku 2010.)

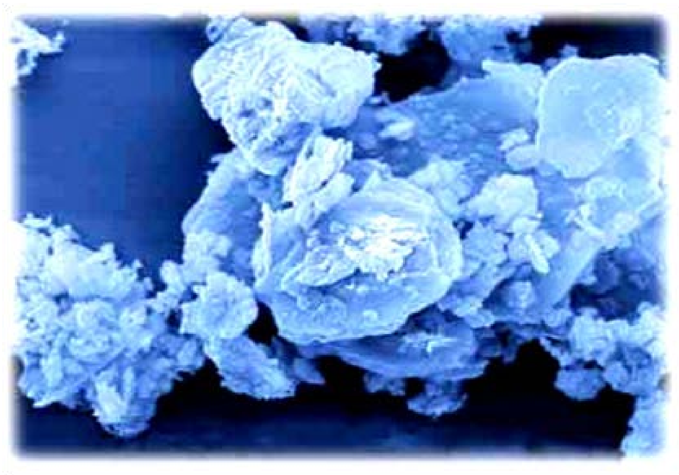

FIGURE 19. Calcined kaolin (Anpeak 2008)

4.6 Titanium Dioxide

Titanium dioxide (*TiO_2*) is a synthetically made specialty pigment. It has two crystal forms which are anatase and rutile. Anatase is more common as filler because rutile is more expensive. (Turku 2010.) The form of titanium dioxide particles is shown in figure 20.

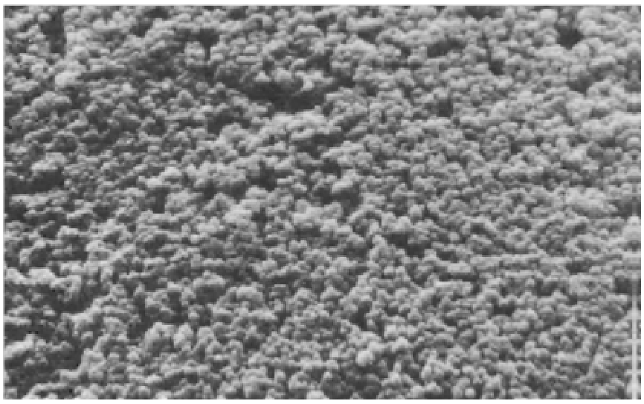

FIGURE 20. Microscope picture of titanium dioxide (Turku 2010)

Brightness and light scattering of titanium dioxide are excellent due to small particle size and cleanliness of the synthetic manufacturing process. Drawback of titanium dioxide is poor retention which can be improved by flocking the particles. Because of the very high price it is generally used as an intensifier and only 5-25 % of the amount of main filler. (Häggblom-Ahnger & Komulainen 2006, 41.)

4.7 Gypsum

Gypsum ($CaSO_4$) which is also known as calcium sulphate is a white powder with high brightness. The color varies from white to light grey. It can be obtained from natural gypsum rock, from industrial processes or from power plants. It is also possible to use gypsum together with calcium carbonate or kaolin clay. Disadvantages of gypsum are high solubility and tendency to plug machine welts. One form of gypsum particle can be seen from figure 21. (Wilson 2006; Krogerus 2007, 63.)

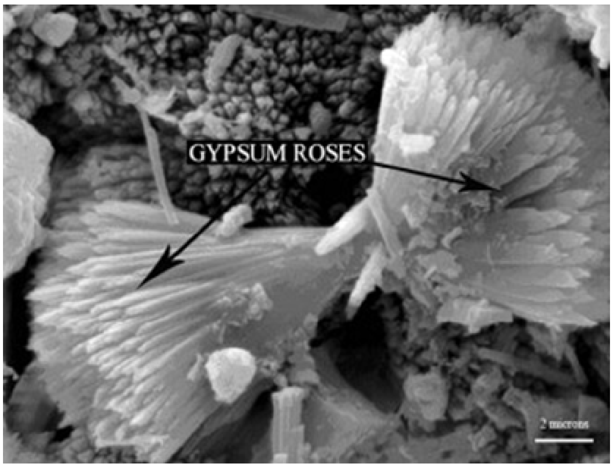

FIGURE 21. Microscopic overlook of rose-like gypsum particles (ScienceDirect 2012)

5 PROSPECTS FOR FILLERS

Replacing mineral fillers by natural starch is one of the outlooks in modern paper making. Technical Research Center of Finland has developed starch-based raw materials which are expected to become international success. The advantages of starch are improved surface strength of the paper, better color rendering and easier achievable gloss. Paper lightens 20-30 % when using starch in filling and coating and therefore also transportation costs decrease. Most remarkable is that the starch-based paper is totally recyclable and the components can be transformed into bio energy without harmful discharge. However, the manufacturing costs are quite high for now. (VTT Technical Research Center of Finland develops high-technology ecological paper 2005.)

Starch consumption has grown 10 % more than paper consumption. Starch should be applied early in the process and the maximum dosage is 0,75 % - 1,5 %. Most effective benefits are achieved when starch is primarily absorbed on fibers or fines. It is also possible to cover fillers by starch to minimize the reduction effects of strength properties. (Krogerus 2007, 77.)

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